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A NEW DENSE FORM OF SOLID GERMANIUM

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A New Dense Form of Solid Germanium

Abstract. A new form of solid germanium, of greater density than ordinary cubic germanium, can be formed by compressing cubic germanium at pressures exceeding 120 kilobars and reducing the pressure back to that of the atmosphere. The crystal structure is tetragonal, with a equal to 5.93 angstroms and c , to 6.98; 12 atoms per unit cell; and theoretical density, 5.91 grams per cubic centimeter. Electrically it behaves like a semiconductor. At temperatures above 200°C it reverts rather rapidly to the cubic form.

A new form of solid germanium has been prepared which has a density about 11 percent greater than that of the ordinary cubic form. It is produced by compressing ordinary cubic germanium, at room temperature, at a pressure in excess of 120 kilobars [at this pressure it is converted to a form that is a high conductor of electricity, as discovered and reported by Minomura and Drickamer (1)], then reducing the pressure back to that of the atmosphere. The material produced in this way is recovered as a solid polycrystalline body of gray metallic appearance.

The new form was discovered after a pressure calibration had been run on a high-compression General Electric belt apparatus (2). In the calibration study a little bar of cubic germanium (0.020 by 0.025 by 0.080 inch) was used as the resistance element, and the transition at pressures greater than 120

kbar was looked for. The remarkable resistance behavior reported by Minomura and Drickamer was observed, as shown in Fig. 1; the transition pressure was consistent with that observed for an iron sample in the same apparatus at 130 kbar (3). The sharp rise of resistance during the unloading (Fig. 1) was interpreted as being the reverse of the transition that took place during loading. However, when the little germanium bar was observed after the run, it appeared to be thinner than before. The best dimensional measurements that could be made indicated that the bar had decreased in volume by roughly 15 percent. Such an increase in density would suggest the presence of a new, more dense form of germanium. Accordingly, an x-ray diffraction study was made to check the structure.

The resulting Debye-Scherrer pattern was that of a crystalline material, different from that of ordinary germanium. It was of considerable complexity and could not be readily indexed. No special effort at interpretation seemed justified until it could be demonstrated that the pattern was that of a single phase and was reproducible. A quick proof that only germanium was present was obtained by heating the specimen to 800°C; the Debye-Scherrer pattern of ordinary cubic germanium was the result. Then, a considerable number of high-compression tests were made, always with the same end product and the same complex pattern. This was true even for tests in which the sample was heated to high temperatures while under pressure exceeding 120 kbar. It was noted that the crystallites must be quite small, since a progressive line broadening with increase in Bragg angle occurred, and since no spottiness in the arcs could be observed when the specimen was stationary during an x-ray exposure.

All the powder lines could be indexed for a tetragonal cell with a equal to 5.93 angstroms and c , to 6.98. With 12 atoms in the unit cell, the theoretical density is 5.91 g/cm³, as compared to 5.32 g/cm³ for ordinary germanium. This density was confirmed by E. L. Simons by means of an ingenious buoyancy method (4), the results of determinations on two samples being 5.86 ± 0.12 and 5.90 ± 0.12 g/cm³. Application of the same buoyancy method to bars of single-crystal cubic germanium of similar size yielded values of 5.32 ± 0.12 g/cm³, in agreement with the theoretical value.

From the systematic absences, the

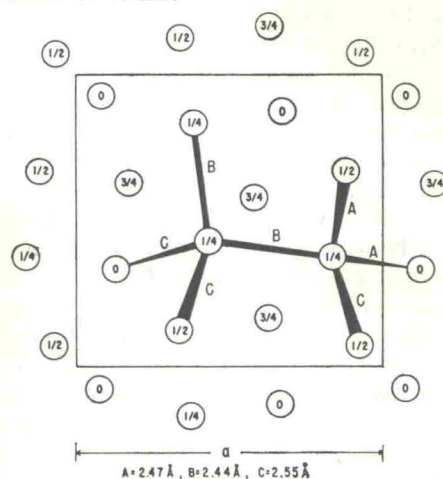


Fig. 2. A projection of the structure of the new dense form of germanium onto (001). The elevations along c (in fractions of the cell length) are given by the numbers inside the circles.

space group $P4_22-D4^8$ (or its enantiomorph $P4_22-D4^4$) is indicated; and with 12 atoms per cell, two sets of positions are called for: 4(a) $xx0$, and so on, and 8(b) xyz , and so on. Approximate values of $x = 0.075$ in 4(a) and of $x = 1/6$, $y = 3/8$, and $z = 1/4$ in 8(b) were found by trial and error to give quite good intensity agreement and to conform to acceptable interatomic distances.

The resulting structure, illustrated in Fig. 2, consists of linkages of rather distorted tetrahedra. The tetrahedral environments of the two kinds of germanium atoms are shown by the bonding scheme in Fig. 2. There are three

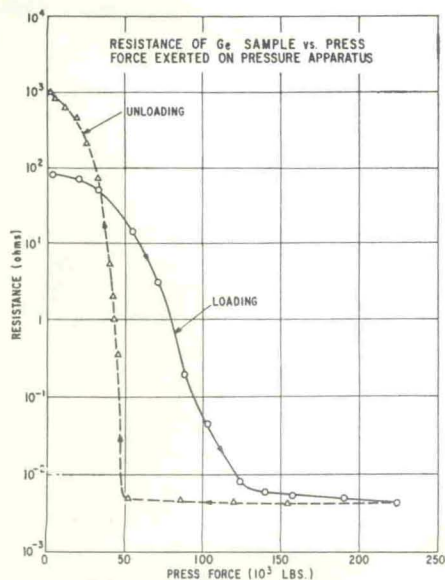


Fig. 1. Plot of resistance versus press force for a germanium sample in a General Electric high-compression belt apparatus.

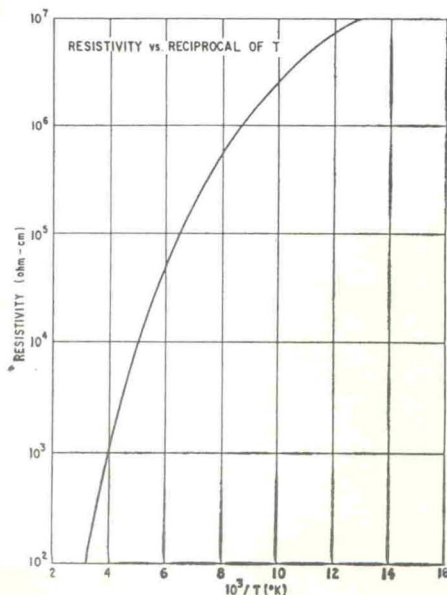


Fig. 3. Plot of resistivity against the reciprocal of absolute temperature for the new dense germanium.

different bond lengths, but they are essentially the same as in ordinary germanium (2.45 angstrom). The bond angles vary from 91 to 120 degrees. At the present stage of investigation the distances and angles have not been very precisely determined.

The new dense germanium proved to be quite stable at room temperature, but at moderately elevated temperatures it reverted to the cubic form. At a temperature of 125°C, about half reverted to the cubic form in 8 hours. At 200°C the dense germanium was transformed almost completely within 6 hours. More measurements of the rate of conversion as a function of temperature will be required to determine the activation energy of transformation from the tetragonal to the cubic form.

Measurements of the resistivity of the new dense material as a function of temperature showed that it behaves as a semiconductor. A typical set of data for low temperatures, obtained by S. J. Silverman, is shown in Fig. 3. Measurements at higher temperatures were meaningless because at these temperatures the material reverted to the cubic form. The dense germanium was tested for superconductivity at cryogenic temperatures by H. R. Hart, Jr. Tests

made at temperatures down to 0.33°K gave no indication of transition to a superconducting state.

It is of interest to establish the relationship of this new dense form of germanium to the highly conducting form found at pressures in excess of 120 kbar. Judging from the resistance behavior—particularly the sharp and great increase in resistance during decompression—one would expect the final state to be different from the highly conducting high-pressure form. In the absence of direct experimental information on the density and crystal structure of the high-pressure phase, and without full experimental phase diagram data, the conclusion that the two forms differ is only tentative. Perhaps the set of transformations reported here in germanium is an example of the reaction mechanism proposed recently by Libby (5).

Meanwhile, we believe the pressure-temperature phase diagram may well be as constructed by Jayaraman *et al.* (6), who took into account the work of Hall (7) on the effect of pressure on the melting point of germanium, and the room-temperature transition of Minomura and Drickamer (1). This diagram calls for a triple point for Ge I

(cubic)/Ge II (high-pressure form)/liquid at 500°C and 115 kbar. The room-temperature transformation at 120 kbar would then be a transformation to a new solid state (Ge II), not a melting phenomenon. In this system, the new dense germanium would be a metastable, low-pressure form, which could be called Ge III (8).

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References and Notes

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8. We gratefully acknowledge the help of R. E. Tuft, who carried out many of the high-pressure runs; of L. M. Osika and Mrs. D. K. DeCarlo, who took most of the x-ray photographs; and of H. Brandhorst, who assisted in the analysis of the diffraction patterns. We are also indebted to L. Apker, the late W. C. Dash, R. N. Hall, F. H. Horn, P. Kennicott, B. W. Roberts, H. M. Strong, D. Turnbull, and R. H. Wentorf, Jr., for valuable discussions and material.

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